Supplementary Material

Nanostructured MnO2 modified TiN nanotube arrays for advanced supercapacitor electrode material

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**Materials and methods**

*Chemicals*: Ti mesh (50 meshes, 99.5% purity) with the thickness of 0.12 mm and 40 wt.% hydrofluoric acid. All reagents are analytical grade and used without further purification.

*Preparation of TONM*: A large piece of raw Ti mesh was cut into square pieces of 2.5 × 2.5 cm2, which were ultrasonically degreased in acetone, isopropanol, and methanol for 15 min, respectively, and then chemically etched in a mixture of HF and HNO3 aqueous solution (HF:HNO3:H2O = 1:4:10 in volume) for 10 s, afterwards rinsed with deionized water and finally dried in air. Electrochemical anodic oxidation was performed at 60 V direct current voltages for 24 h in DEG solution containing 1.5 vol.% HF, using Ti mesh as the working electrode and Pt plate as counter electrode. The as-prepared samples were ultrasonically rinsed with deionized water and dried in air.

*Preparation of TNNM*: TONM samples in a quartz boat were placed in the heating center of a horizontal quartz tube vacuum furnace. Prior to heating, the system was evacuated and flushed with high pure N2 to eliminate oxygen. Afterwards, the furnace was heated in N2 to 750 °C, and then changed to NH3 flow keeping a flow rate of 100 mL min-1 for 5 h while the temperature was maintained. Finally, the furnace cooled down to room temperature in N2.

*Preparation of MnO2 modified TNNM*: Different precursor solutions were employed for synthesizing MnO2 nanostructures by hydrothermal synthesis method. A TNNM sample was placed at the bottom of the reaction solution in sealed 150 mL Teflon-lined autoclave, which was put into a muffle furnace for hydrothermal reaction. The solution compositions and reaction conditions are summarized in Table S1.

Table S1. The precursor solution compositions and hydrothermal reaction conditions for preparing nanostructured MnO2.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Solution | KMnO4 | MnSO4·H2O | HCl | H2O | Temperature  [°C] | Time  [h] | Sample |
| M-1 | 0.875 g | 0.35 g | - | 70 mL | 140 | 3 | TN-MO-SS |
| 12 | TN-MO-S |
| 18 | TN-MO-SR |
| M-2 | 1.106 g | - | 0.88 mL | 70 mL | 150 | 6 | TN-MO-RS |
| M-3 | 0.7875 g | - | 1.75 mL | 70 mL | 150 | 12 | TN-MO-R |

*Characterization*: The crystalline phase compositions of the samples were measured by a Rigaku D/Max 2550VB3+/PC X-ray diffractometer (XRD) equipped with graphite monochromatized Cu Kα radiation (λ = 0.15405 nm). Nanostructures and elemental distributions of the samples were characterized by a Schottky field emission scanning electron microscopy (FESEM, FEI Nova NanoSEM 450) equipped with energy dispersive spectroscope (EDS, EDAX).

*Electrochemical performance measurement*: Electrochemical measurements were carried out with CHI660E electrochemical three-electrode system in 2 mol L-1 KCl solution, where the samples acted as the working electrode, Pt foil acted as the counter electrode, and Ag/AgCl electrode acted as the reference electrode. Cyclic voltammetry (CV) curves were obtained in a voltage range from -0.2 V to 0.8 V at different scan rates of 5, 10, 20, 40, 60, 80 and 100 mV s-1, respectively. Galvanostatic charge/discharge curves were recorded in a potential window from -0.2 V to 0.8 V at a series of current densities. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency from 100 kHz to 10 mHz at an open-circuit potential vibration of 5 mV.



Figure S1. Schematic diagrams of MnO2 nanostructure growth process.



Figure S2. Schematic diagrams of δ-MnO2 and α-MnO2 crystal structure.



Figure S3. XRD pattern (a) and SEM images (b-e) of TN-MO-S-500.